

Elastic Properties of Single-Wall Nanotubes

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We report results of theoretical studies on the elastic properties of single-wall nanotubes of the following compositions: C, BN, BC₃, BC₂N and C₃N₄. These studies have been carried out using a total energy, non-orthogonal tight-binding parametrisation which is shown to provide results in good agreement both with calculations using higher levels of theory and the available experimental data. Our results predict that of all types of nanotubes considered, carbon nanotubes have the highest Young's modulus. We have considered tubes of different diameters, ranging from 0.5 to 2 nm, and find that in the limit of large diameters the mechanical properties of nanotubes approach those of the corresponding flat graphene-like sheets.

The discovery of C₆₀ and fullerenes [1] in the mid 80's was soon followed by the observation of nanotubes [2], first reported by Iijima [3] in 1991. Since then nanotubes have been the focus of attention of a growing scientific community, attracted to them by their many interesting properties, such as their structure, electrical conductivity and mechanical properties, as well as by their large potential for practical applications. Two types of nanotubes exist: those originally observed by Iijima [3] were multi-wall nanotubes (MWNT's), formed by concentric shells of apparently seamless cylinders of graphene, having a separation between them similar to that in graphite. More recently, single-wall nanotubes (SWNT's) have also been synthesized. As their name indicates, these consist of a single seamless cylinder of graphene [2].

Soon after the discovery of carbon nanotubes it was proposed that other compounds forming graphite-like structures, such as BN [4], BC₃ [5], BC₂N [6], and CN [7], could also form nanotubular structures. Indeed BN [8–10], BC₃ and BC₂N [11] have now been synthesized, though the actual structure of BC₂N tubes seems to correspond to concentric shells of C and BN in a 'sandwich' structure [12]. Other tubular structures formed by heavier element compounds have been predicted, such as GaSe [13], and synthesized, like WS₂ and MoS₂ [14].

In this paper we focus our attention on the structural, energetic and mechanical properties of single-wall carbon and composite nanotubes. We perform a systematic study of these systems using Tight-Binding total energy methods [15], as well as first-principles [16] calculations. Some of the results reported here have already appeared in published form [17], but we also provide previously unpublished results for the C₃N₄ nanotubes.

The structure of this paper is as follows. In Sec. I we review the available experimental data on the mechanical properties of nanotubes, while Sec. II is devoted to discussing previous theoretical work. In Sec. III we describe the models used in our work and the calculations carried out in order to address the issues discussed here. Then, in Sec. IV we discuss our results and conclusions.

I. REVIEW OF EXPERIMENTAL RESULTS

There is a growing body of experimental evidence indicating that carbon nanotubes (both MWNT's and SWNT's) have extraordinary mechanical properties. There are many direct observations of the large bending flexibility [18–20] of nanotubes, which provide evidence of their capability to sustain large strains without evidence of collapse or failure. However, the technical difficulties involved in the manipulation of these nano-scale structures makes the direct determination of their mechanical properties a rather challenging task. In spite of these difficulties, a number of experimental measurements of the Young's modulus of nanotubes have been reported. The first such study was that of Treacy *et al.* [21], who correlated the amplitude of the thermal vibrations of the free ends of anchored nanotubes as a function of temperature with the Young's modulus. Regarding a MWNT as a hollow cylinder with a given wall thickness, one can obtain a relation between the amplitude of the tip oscillations in the limit of small deflections, and the Young's modulus. Having quantified the amplitude of those oscillations by means of careful TEM observations of a number of nanotubes, Treacy *et al.* were able to obtain an average value of 1.8 TPa for the Young's modulus, though there was significant scatter in the data (from 0.4 to 4.15 TPa for individual tubes). Thus this number is subject to large error bars, but it is nevertheless indicative of the exceptional axial stiffness of these materials.

More recently Krishnan *et al.* [22] have reported studies on SWNT's using the same technique. A larger sample of nanotubes was used, and a somewhat smaller average value was obtained, $Y = 1.25$ TPa, closer to the expected value for graphite along the basal plane.

This technique has also been used by Chopra and Zettl [23] to estimate Y for BN nanotubes. Their results indicate that these composite tubes are also exceptionally stiff, having a value of Y around 1.22 TPa, very close to the value obtained for carbon nanotubes.

Another way to probe the mechanical properties of

nanotubes has been described by Wong *et al.* [24], who have used the tip of an Atomic Force Microscope (AFM) to bend anchored MWNT's while simultaneously recording the force exerted by the tube as a function of the displacement from its equilibrium position, information from which the Young's modulus of the nanotube can be extracted. Wong *et al.* have reported a mean value of 1.28 TPa, which is in good agreement with the previous experimental results. Also Salvétat and coworkers [25] have used a similar idea, which consists of depositing MWNT's on an ultra-filtration membrane. Many tubes are then found to lie across the holes present in the membrane, with a fraction of their length suspended. The tip of an AFM is then used to exert a load on the suspended length of the nanotube, measuring at the same time the nanotube deflection. The mean value of the Young's modulus obtained by Salvétat *et al.* was 0.81 TPa. A similar procedure has also been used by Muster *et al.* [26], who used an AFM to record the profile of a MWNT lying across an electrode array. By assuming a simple Van der Waals interaction law between the tube and the substrate, and regarding the nanotube as an elastic beam, the measured profile was found to be consistent with a Young's modulus of approximately 1 TPa.

Other experiments, which as yet have not aimed at the mechanical characterization of nanotubes, nevertheless hint at other possible ways in which this characterization could be carried out. Among these we could cite the embedding of nanotubes in resins [27], or measuring the bending of anchored nanotubes in controlled magnetic fields [28].

All these experiments have contributed to confirming that nanotubes, both SW and MW, have indeed exceptional mechanical properties, but there are still questions that remain unresolved. The work of Chopra and Zettl [23] indicates that BN nanotubes are close in stiffness to carbon nanotubes, but the experimental error bars are too large to state categorically that one type of tube is stiffer than the other. The results of Salvétat *et al.* [25] clearly indicate that MWNT's synthesized by the arc-discharge method [29] are much stiffer than those produced by the catalytic decomposition of hydrocarbons [30], which have a Young's modulus in the range of 10-50 TPa. This large difference is presumably a reflection of the influence of the high density of defects present in the structure of the latter tubes, but a detailed quantification of the influence of defects on the mechanical properties of nanotubes is as yet missing.

II. PREVIOUS THEORETICAL WORK

The mechanical properties of nanotubes have been addressed also by means of theoretical calculations in a number of publications [18,31-37]. Most of these studies have been carried out using empirical potentials, al-

though tight-binding based models have also been occasionally used [33]. Though well-tested empirical potential models exist for carbon-based systems [38-40], to our knowledge no such model exists for the composite systems, and therefore these materials have been mostly studied using first-principles methodologies [4,5]. However, these latter studies have concentrated largely on electronic, structural and vibrational properties of the composite systems, without addressing the issue of their mechanical properties.

Lu [37] has reported an extensive study of the Young's modulus, Poisson ratio and elastic constants of carbon nanotubes (both SW and MW, as well as ropes of SWNT's) using an empirical pair potential. Yakobson *et al.* [34] and Nardelli *et al.* [35] have studied the behaviour of nanotubes subject to large axial strains.

III. MODEL AND CALCULATIONS

For the majority of the calculations reported here we have used a non-orthogonal Tight-Binding scheme due to Porezag and coworkers [41]. Tight-Binding (TB) methods [15] lie in the centre region of the spectrum of simulation methods in both computational cost and reliability. Empirical potentials [38] are much cheaper to use, but their accuracy and reliability is often questionable. First-principles methods [16] on the other hand are more reliable, but their computational demands are orders of magnitude larger than for TB calculations, and often this makes their use impractical.

The TB model of Porezag *et al.* [41] contains two contributions to the total energy: a so-called *band-structure* energy term, and a repulsive pair-potential. The band-structure energy is calculated as the sum of the eigenvalues of the occupied states of a TB Hamiltonian. A matrix representation of this Hamiltonian is constructed using a minimal basis set consisting of a single atomic-like orbital per atomic valence state. The matrix elements are evaluated in the framework of Density Functional Theory (DFT) (normally in the Local Density Approximation, LDA), but retaining only two-centre contributions to the integrals. This means that each matrix element of the Hamiltonian depends only on the relative distance of the two atoms on which the corresponding basis functions are centred and the direction cosines of the internuclear vector [42,15]. Since the basis set is not orthogonal, the calculation of the band structure energy requires the solution of a generalized eigenvalue problem [43]. The repulsive pair potential is then constructed in such a way that the total TB energy of a reference system (usually the dimer) matches that of the full DFT calculation with the same basis set. For more details on the construction of the model the reader should consult the original references [41], but an important point worth emphasizing

here is the fact that no information concerning the mechanical properties of the system under study are used in the construction of the TB parametrisation.

Even though the TB model used here is not fitted to any empirical data, it is nevertheless approximate and less accurate than conventional first-principles methods. For this reason we have also carried out plane-wave (PW) pseudopotential DFT calculations for the (6,6) C and BN nanotubes, in order to have the possibility of comparing our TB results with fully *ab initio* calculations. The PW calculations were performed using Troullier-Martins pseudopotentials [44] with a PW cutoff of 40 Ry for the basis set, and 10 reciprocal space points generated according to the Monkhorst-Pack scheme [45] to sample the one-dimensional Brillouin zone. The TB calculations used Γ -point sampling only, but the periodic cells were chosen large enough as to ensure the same degree of convergence in total energy differences as were achieved in the PW calculations.

As we have seen in Sec. I, the central property characterizing the stiffness of nanotubes, to which the experiments have access, is the Young's modulus. In bulk 3-D systems Y is given by the following expression:

$$Y = \frac{1}{V_0} \left(\frac{\partial^2 E}{\partial \epsilon^2} \right)_{\epsilon=0}, \quad (1)$$

where E is the total energy, ϵ is the strain and V_0 is the equilibrium volume. The second derivative measures how rapidly the energy grows as the system is distorted out of its equilibrium configuration. Usually Y is given in units of pressure, and this is why the factor of V_0^{-1} appears in this formula. However, Eq. (1) presents an ambiguity in the case of SWNT's, which stems from the definition of V_0 . To define V_0 for a SWNT one needs to specify the wall thickness, and there is no clear way to define the thickness of a wall one-atom thick. In previous publications different authors have used different values for the tube wall thickness, though the most common convention has been to adopt the value of the interlayer spacing in graphite. Nevertheless the value of Y depends on the inverse of the wall thickness δR , and is therefore rather sensitive to the chosen value. In a recent publication [17] we proposed a way to bypass this problem by using an alternative definition of the Young's modulus, more appropriate to the case of SWNT's:

$$Y_s = \frac{1}{S_0} \left(\frac{\partial^2 E}{\partial \epsilon^2} \right)_{\epsilon=0}. \quad (2)$$

Here S_0 is the surface area defined by the nanotube at zero strain, which is a well defined quantity. Given that $V_0 = S_0 \delta R$, one can recover the usual definition by simply dividing by δR : $Y = Y_s / \delta R$, if one wishes to adopt a particular convention.

Another mechanical property of interest is the *Poisson ratio*, σ , which is defined by

$$\frac{R - R_{eq}}{R_{eq}} = -\sigma \epsilon, \quad (3)$$

where R is the radius of the tube at strain ϵ , and R_{eq} is the equilibrium (zero strain) tube radius. The Poisson ratio measures how much the tube contracts (expands) radially when subject to a positive (negative) axial strain ϵ .

We have performed a series of calculations using the Tight Binding model discussed above aimed at determining Y_s and σ of both carbon and composite SWNT's, including BN, BC₃, BC₂N and C₃N₄ nanotubes. Two different graphite-like BC₂N structures are possible, but in our studies we have only considered the structure known as II, since this is the one reported to be most stable [46].

The calculations consist of taking a section of a nanotube using periodic boundary conditions to simulate an infinite tube, and subject it to both negative and positive strains along the axial direction. At each strain the positions of all atoms in the repeat-cell are fully relaxed without constraints, using the Conjugate Gradients minimisation technique [43]. A given calculation was assumed to have converged once the total energy varied less than 10^{-5} Hartree between two successive iterations. From these calculations we obtained the total energy and atomic positions as a function of the axial strain imposed on the nanotube, from which we could calculate Young's modulus and the Poisson ratio, as well as the equilibrium structures of each nanotube considered.

IV. RESULTS AND DISCUSSION

Let us first consider the difference of energy between a nanotube structure and the corresponding infinite flat graphene sheet. This energy difference is known as the *strain energy* E_s , and we have plotted it in Fig. 1 for C, BN and BC₃ (n,n) nanotubes, as a function of the tube diameter. It can be seen from Fig. 1 that the strain energy varies as D^{-2} , where D is the tube diameter; we have performed fits of functions of the form aD^{-b} to the data, and the values for the parameters a and b are given in Table I.

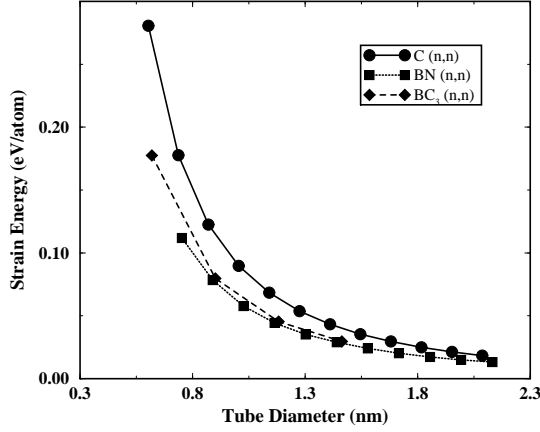


FIG. 1. Curvature strain energy as a function of the equilibrium tube diameter, as obtained from the tight-binding calculations, for C, BN and BC₃ nanotubes.

That the strain energy should decay as D^{-2} was predicted by Tibbetts [47] (see also Mintmire and White [48]) on the basis of continuum elasticity theory, according to which the strain energy per atom is given by

$$\frac{E_s}{N} = \frac{Y a^3}{6} \frac{\Omega}{D^2}, \quad (4)$$

where Y is the Young's modulus of the tube, a is a constant of the order of the inter-layer spacing in graphite and Ω is the area per atom. Note that from Eq. (4) and the numerical fits to the strain energy data of Fig. 1 given in Table I, one can predict that the Young's modulus of SWNT's of BN and BC₃ of a given diameter should be approximately 0.68 and 0.71 respectively that of a carbon nanotube of the same diameter. As we shall see below, direct calculations of Young's modulus for these tubes obey approximately this relation.

$B_x C_y N_z$	(n,m)	$a \times 10^2$ (eV nm ² /atom)	b
C	(n,n)	8.1	2.083
	(n,0)	8.7	1.996
BN	(n,n)	5.5	1.984
	(n,0)	5.6	1.980
BC ₃	(n,n)	5.8	1.984
	(n,0)	5.6	2.048

TABLE I. Parameters obtained from fitting the strain energy curves of Fig. 1 to a function of the form aD^{-b} . Note that the value of b is very close to 2 in all cases.

$B_x C_y N_z$	(n,m)	D_{eq} (nm)	σ	Y_s (TPa · nm)	Y (TPa)
C	(10,0)	0.791	0.275	0.416	1.22
	(6,6)	0.820	0.247	0.415	1.22
		(0.817)		(0.371)	(1.09)
	(10,5)	1.034	0.265	0.426	1.25
	(10,7)	1.165	0.266	0.422	1.24
	(10,10)	1.360	0.256	0.423	1.24
	(20,0)	1.571	0.270	0.430	1.26
	(15,15)	2.034	0.256	0.425	1.25
BN	(10,0)	0.811	0.232	0.284	0.837
	(6,6)	0.838	0.268	0.296	0.870
		(0.823)		(0.267)	(0.784)
	(15,0)	1.206	0.246	0.298	0.876
	(10,10)	1.390	0.263	0.306	0.901
	(20,0)	1.604	0.254	0.301	0.884
	(15,15)	2.081	0.263	0.310	0.912
BC ₃	(5,0)	0.818	0.301	0.308	0.906
	(3,3)	0.850	0.289	0.311	0.914
	(10,0)	1.630	0.282	0.313	0.922
	(6,6)	1.694	0.279	0.315	0.925
BC ₂ N II	(7,0)	1.111	0.289	0.336	0.988
	(5,5)	1.370	0.287	0.343	1.008
C ₃ N ₄	(6,0)	0.913	0.280	0.192	0.565
	(8,0)	1.210	0.238	0.207	0.610
	(6,6)	1.558	0.177	0.228	0.670
	(8,8)	2.075	0.132	0.233	0.684

TABLE II. Structural and elastic properties of selected nanotubes obtained from the tight-binding calculations reported here. Young's modulus values given in parenthesis were obtained from first-principles calculations. Also the value of Y with the convention $\delta R = 0.34$ nm is given for comparison.

A first indication that the TB model used in this work is a reliable one stems from the good agreement obtained in the strain energy as calculated here and that calculated from first-principles methods and reported elsewhere [4,5]. Another indication comes from the fact that a certain buckling on the surface of the BN nanotubes is predicted to occur, also in agreement with preliminary first-principles calculations [4]. This buckling, which results from the B atoms displacing inwards towards the tube axis, while the N atoms displace in the opposite direction, is a consequence of the slightly different hybridizations of B and N on the curved surface of the nanotube. The amount of buckling is dependent on the tube diameter, but it is otherwise independent of the tube structure for arm-chair and zig-zag nanotubes.

In Table II we give the obtained values of structural and mechanical properties for a set of nanotubes obtained from our calculations. For comparison we also give results for the (6,6) C and BN nanotubes calculated with PW pseudopotential DFT calculations. As can be seen, the agreement between the TB and first-principles calculations in both structural and mechanical properties is rather good. Notice also that the values of Y_s (and in fact those of Y also) for C, BN and BC_3 nanotubes of similar diameters are approximately in the same ratio as predicted from Eq. (4).

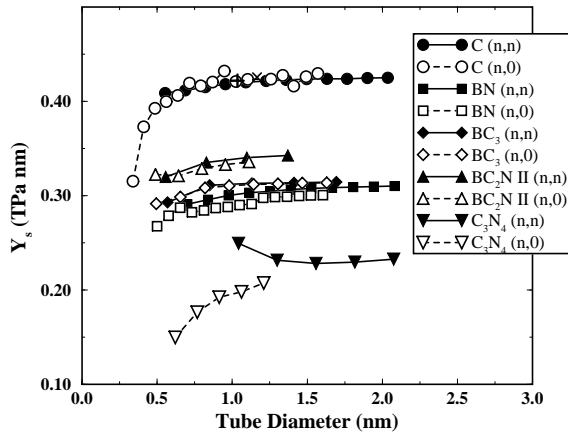


FIG. 2. Young's modulus as a function of the tube diameter for C, BN, BC_3 , BC_2N (structure II only) and C_3N_4 , as calculated from the tight-binding simulations. Results obtained for (n,n) nanotubes (filled symbols), (n,0) nanotubes (empty symbols) and also for C (10,5) (+) and (10,7) (x) are shown.

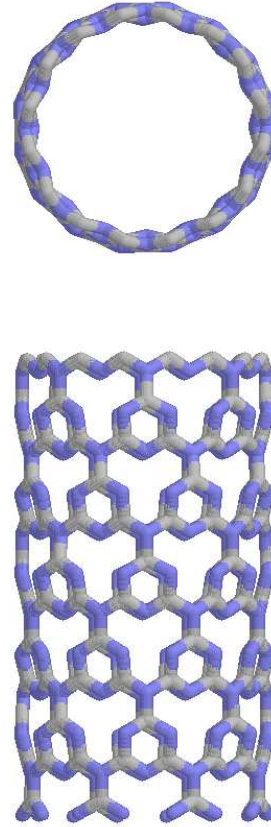


FIG. 3. Relaxed structure for the C_3N_4 (8,0) nanotube, as obtained from the TB calculations. The dark shaded atoms are Nitrogen atoms, while the lighter ones are Carbon atoms.

In Fig. 2 the values Y_s have been plotted as a function of the tube diameter for the different types of tubes considered in this work. The first observation that can be extracted from Table II and Fig. 2 is the fact that carbon nanotubes are predicted to have the highest Young's modulus of all the different types of tubes considered. BN and BC_3 tubes have very similar values of Y_s , though the latter have slightly larger values. The BC_2N nanotubes are predicted to be slightly stiffer than the BN and BC_3 tubes, while C_3N_4 nanotubes lie well below the rest in stiffness. The value of Y_s we obtain for the wider C nanotubes, 0.43 TPa nm, corresponds to a Young's modulus of 1.26 TPa in the conventional definition of Eq. (1), if we take $\delta R = 0.34$ nm, i.e. the inter-layer spacing in graphite. This value is in very good agreement with the experimental value recently obtained by Krishnan and coworkers [22] for SWNT's (1.25 TPa). It is also in rather good agreement with the value of 1.28 TPa reported by

Wong *et al.* [24], though this later value was obtained for MWNT's. However, it is expected that the Young's modulus be mostly determined by the intra-wall C-C bonds, and it is therefore not surprising that the values look so similar for both MW and SWNT's. For composite nanotubes, the only experimental data on mechanical properties currently available to our knowledge are the results of Chopra and Zettl [23], who have measured Y for BN MWNT's. They quote a value of 1.22 TPa, which is somewhat larger than the result we obtain for these tubes, but nevertheless the agreement is close. Though it may seem that the choice $\delta R = 0.34$ nm is somewhat arbitrary, it should be pointed out that the experimental results are not free of this arbitrariness either, given that to obtain a value of the Young's modulus according to Eq. (1), it is necessary to interpret the experimental observations on the basis of some mechanical model, usually a hollow cylinder with a certain wall thickness. Clearly, in the case of SWNT's the question of how to choose $\delta R = 0.34$ nm applies to experiments as well as to theoretical calculations.

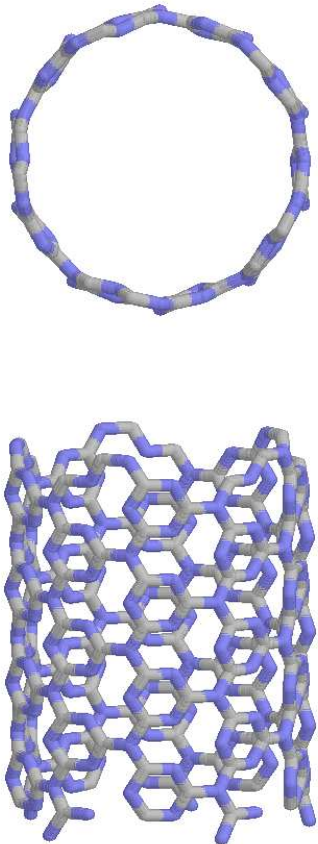


FIG. 4. Relaxed structure for the C_3N_4 (5,5) nanotube.

The reason why C_3N_4 nanotubes are predicted to be so much softer than all other types of nanotubes considered in this work is the fact that for a given amount of tube surface, tubes of this composition have a smaller density of chemical bonds. Indeed, these tubes present a more hollow structure when compared to the other, perfectly hexagonal nanotubes (see Figs. 3 and 4). It is also interesting to note that, while C, BN, BC_3 and BC_2N nanotubes do not show noticeable differences for the structural or mechanical properties as the chiral angle is varied, sizeable differences are observed in the case of C_3N_4 nanotubes. It can be seen in Table II that the (n,n) C_3N_4 tubes have a higher Young's modulus than the (n,0), though both seem to converge towards the same number in the limit of large diameters. This difference is also reflected in the structure, as can be seen in Figs. 3 and 4. Notice how the hexagons are at an angle with the surface of the tube which is different in (n,n) and (n,0) tubes.

As for comparison with other theoretical predictions, the results quoted by Lu [37] are somewhat smaller than ours. The results in ref. [37] are 0.97 TPa for all tubes. This difference is most likely due to the different approaches (empirical potentials and TB) used in that work and ours. We also observe in our results for Y_s a slight dependence on the tube diameter. As the diameter becomes larger, Y_s approaches a plateau value which corresponds to the value calculated for the flat graphene-like sheet of each nanotube composition. Interestingly, the approach to the limit value is from below, as can be expected if one considers that bending a flat graphene sheet weakens the bonds. Given that it is the strength of the chemical bonds which determines the actual value of the Young's modulus, it is natural that small-diameter (high curvature) tubes have smaller Young's moduli, and in the limit of large diameters, the mechanical properties essentially correspond to those of the flat graphene sheet. In contrast, the results of Lu [37] are largely insensitive to the tube diameter. This is due to the fact that pair-potential models, such as the one used by Lu, do not reflect the changing nature of the chemical bonding as the curvature is changed. To reproduce this effect, a model sensitive to the changing environment (i.e. a *many-body* model) is required.

To summarize, we have used a non-orthogonal TB model parametrised for C, B and N based systems to perform a systematic study of the energetic, structural and mechanical properties of single-wall nanotubes of different chemical composition. We have checked the accuracy of our predictions against some first-principles calculations, and the agreement obtained is good. Furthermore, we obtain good agreement with the available experimental data. We obtain strain energy vs. diameter curves which obey very closely the expected D^{-2} be-

haviour. Our results show that carbon nanotubes are expected to be stiffer than any of the composite nanotubes considered, having a Young's modulus of approximately 1.3 TPa, which corresponds to that of a flat graphene sheet within the same theoretical model. The C_3N_4 nanotubes, which present a more hollow structure than the other tubes, are predicted to have a Young's modulus nearly half that of the carbon nanotubes.

We are grateful to G. Seifert and T. Heine for providing the TB parametrisations used in this work. J.A. Alonso, M.J. López and M. Galtier are gratefully acknowledged for helpful discussions. This work was carried out within the framework of the EU Transfer and Mobility of Researchers Namitech project under contract No. ERBFMRX-CT96-0067 (DG12-MITH) and Grant No. DGIS-PB95-0202 of the Spanish Ministry of Education. The use of computer facilities at C4 (Centre de Computació i Comunicacions de Catalunya) and CNUSC (Montpellier) is also acknowledged.

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